White Paper

Munitions in the Underwater Environment: State of the Science and Knowledge Gaps

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EXECUTIVE SUMMARY

SERDP and ESTCP hosted a meeting on Monday, November 30, 2009, to assess the status of various elements needed to evaluate risk associated with munitions in the underwater environment. The main objective of this meeting was to evaluate the adequacy of modeling capability and data sources needed to make defensible risk-based decisions regarding underwater munitions. The elements that are of interest include:

- Site Characterization
- Receptors
- Mobility of Munitions
- Corrosion
- Release Rate
- Fate and Transport
- Ecotoxicity

The assessment includes both chemical and conventional munitions that have been either disposed or fired and are resident in both deep and shallow water environments. There are methods available for evaluating explosive risk and this evaluation is not intended to address that risk. The purpose of this white paper is to summarize the meeting discussion by documenting capabilities that currently exist, and identifying where advancements are needed. Additional goals of this white paper are to both aid the user community in conducting currently mandated assessments and guide future research investments.

The participants at the meeting identified several top level recommendations to assist in future risk assessments and site decisions regarding underwater munitions. These recommendations are listed below:

1. Conduct field data collections on several worst-case underwater munitions sites.
2. Utilize the data to support integrated ecological risk assessments using components available now.
3. Collect data in single field efforts to support available components of risk assessment using a standardized approach to field data collection at underwater sites.
4. Recommend increased working level communication between various agencies and Services investing in research, development, and demonstrations related to munitions in the underwater environment.
5. Investigate approaches used internationally for munitions response and domestically for radioactive sites to identify processes potentially applicable to an underwater munitions risk assessment.

1.0 UNDERWATER MUNITIONS SITES OVERVIEW

As a result of past military training and weapons testing activities, munitions are present at thousands of current and former Department of Defense (DoD) sites encompassing millions of acres. Many active and former military installations have ranges and training areas that include adjacent water environments such as ponds, lakes, rivers, estuaries, and coastal ocean areas.

Within the Formerly Used Defense Sites (FUDS) program alone, the Army Corps of Engineers (USACE) has identified more than 400 sites totaling more than 10 million acres potentially containing munitions in underwater environments. The U.S. Navy and U.S. Marine Corps' munitions response program has identified an additional 33 sites containing munitions. The inventory includes sites that date back to the 18th century and some that were used as recently as the 1990s. Current Navy policy is to include sites into the Navy's Munitions Response Program if those sites are covered by water no deeper than 120 feet deep. Figure 1 presents known or suspected ranges within tidal and inland water areas.

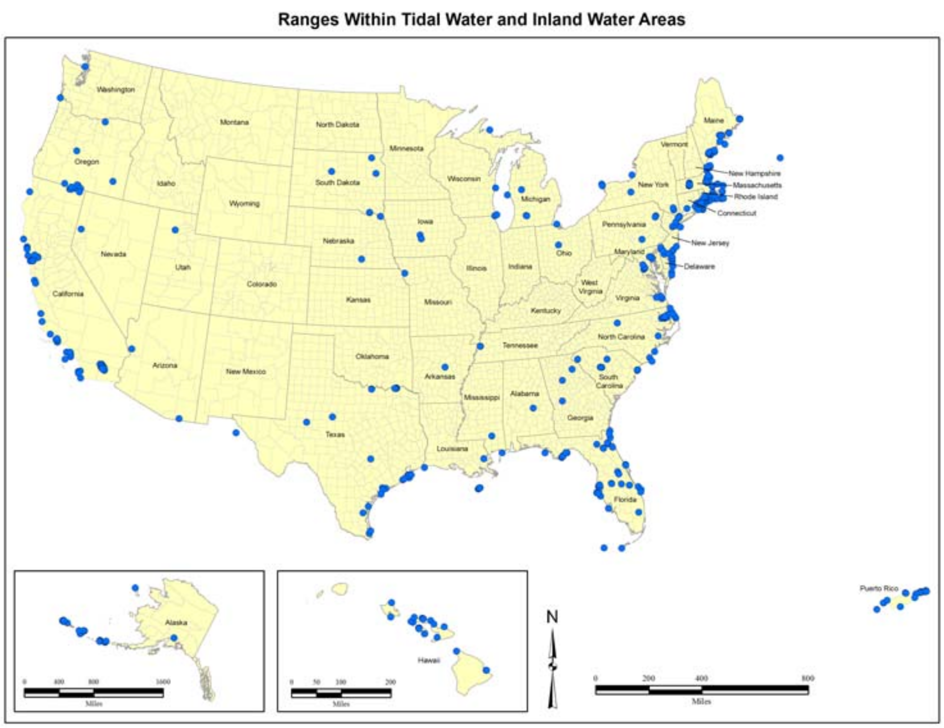

Figure 1. United States Ranges within Tidal and Inland Water Areas

1.1 SITE TYPES

Munitions were fired or disposed of using various methods at numerous underwater sites. The sites containing underwater munitions include ranges and target areas with a variety of surface and subsurface munitions, defense sites including forts and coastal artillery batteries, ocean disposal operations prior to 1972, acts of war such as combat sites or sunken vessels, accident sites, and former manufacturing and handling sites for military munitions and open burning/open

detonation (OB/OD) practices. Ranges and targets include coastal defense sites, island targets, ranges that were previously land targets and were flooded, and littoral training areas.

Currently, the most accurate references on range and site locations include FUDS reports, the Munitions Response Site Inventory in the Defense Environmental Programs Annual Report to Congress (http://deparc.xservices.com/do/mmrp), service historical offices, and nautical charts.

The level of location accuracy for munitions from mobile firing points, bombing ranges, and disposal sites are more varied than fixed firing points. Historical disposal site information often provides only general locations and, when positions are provided, they are typically only accurate to the nearest minute, potentially complicating any attempt to locate the cited munitions.

The most up-to-date data on locations and quantities of disposal sites is found in the appendix on sea disposal of military munitions in the current Defense Environmental Programs Annual Report to Congress (www.denix.osd.mil). The FY08 Report to Congress identified 30 sea disposal sites. In addition, Congressional Research Service Report RL33432 (2007) titled, U.S. Disposal of Chemical Weapons in the Ocean: Background and Issues for Congress, provides an overview of the issues related to munitions disposal. The Army and Navy have organized their data on ocean disposed munitions into a working database that contains historical data on munitions disposals and accidents and assists in identifying areas where use presents a concern.

1.2 SITE CONDITIONS

Underwater munitions sites encompass a wide variety of environments, including near-shore and off-shore ocean, swamps, rivers, and lakes which are complex in nature and chemistry. These sites have a vast array of characteristics such as depth, temperature, salinity, bathymetry, and sediment type, all of which can vary with time.

Much of this site data is available in varying degrees of fidelity, and has to be complied from a variety of separate sources such as National Oceanic and Atmospheric Administration (NOAA), State Department of Natural Resources, or the Minerals Management Service. The data ranges from quite reliable at a regional level to approximate, depending on the type of available data. In addition, a database of possible underwater munitions sites has been developed in Microsoft Access which consists of data from a variety of sources including FUDS and Former Navy Sites. This database includes over 420 ranges at 114 sites and is populated, as available, with: depth, substrate, wave exposure, geomorphology, acreage, munitions items, tides, currents, sediment type, salinity, and slope. The draw back of this database is that there are limited data for many sites which restricts its utility, but there is the potential for developing this system as a comprehensive tool.

1.3 MUNITIONS CONDITIONS

Underwater sites may contain a variety of munitions types, including bombs, projectiles, mortars, grenades and rockets. Information can be gathered on the munitions types, quantity, age, and distribution by investigating historical Service records concerning range use or disposal method. Records on specific munitions used or disposed and quantities are generally incomplete. There is also a high degree of uncertainty concerning quantities present at most, if not all, sites. Some of

this information can be gathered through site characterization field surveys. For example, if a range had a known fixed firing position, the distribution will likely exhibit a predicable pattern that can be verified with a geophysical sensor transect survey. Fixed firing points generally provide a greater degree of accuracy in determining likely distribution.

Specific munitions type characteristics such as material composition, wall thickness, and fillers are available in the Munitions Items Disposition Action System (MIDAS). Munitions constituents (MCs) can be identified through the known munitions type. The MIDAS and technical libraries for specifications on munitions can be referenced to collect this information.

Physical and chemical properties of the MCs and their toxicity and environmental fate can be gathered from Environmental Protection Agency (EPA) databases and technical journals. There is also a report available on modeling chemical agent releases of disposed munitions, The Ocean Dumping of Chemical Munitions: Environmental Effects in Arctic Seas, 1997 (www.foia.cia.gov).

1.4 RECEPTORS

Basic information on the human use and ecology of an area is readily accessible from a variety of sources. Demography and use information is often available from the state department of natural resources, Minerals Management Service, NOAA, and the U.S. Census Bureau. Commercial fish landing data is typically collected by state governments as part of their resource management programs and is available but the level of detail varies. For instance, data is only available for some fish by species.

NOAA has benthic habitat information and environmental sensitivity index maps available for coastlines. The presence of threatened or endangered species is available from the Fish and Wildlife Service and state natural heritage programs.

2.0 MODELING CAPABILITIES AND DATA SOURCES: STATE OF THE SCIENCE AND KNOWLEDGE GAPS

The objective of the November 30, 2009 meeting was to evaluate the adequacy of modeling capabilities and data sources needed to make defensible risk-based decisions regarding underwater munitions. Elements of interest include:

- Mobility of Munitions
- Corrosion
- Release Rate
- Fate and Transport
- Ecotoxicity

The following sections will describe the current state of the science and knowledge gaps for each of these elements.

2.1 MUNITIONS MOBILITY PREDICTION

The evaluation of munitions mobility in the underwater environment has the potential to support risk assessment analyses and site management decisions. Physical characteristics of the munitions and environmental conditions at a site may be used as inputs to models that determine whether munitions can be expected to be stationary or mobile.

The Naval Facilities Engineering Command–Engineering Service Center (NAVFAC-ESC), with funding from the Navy Environmental Sustainability Development to Integration (NESDI) program, initiated an ESTCP project *Predicting the Mobility and Burial of Underwater Munitions and Explosives of Concern Using the VORTEX Model* (MM-0417) to modify the existing Vortex Lattice model (VORTEX), used to predict mine mobility and burial, to predict Unexploded Ordnance (UXO) mobility and burial in the underwater environment. The new software is called the UXO Mobility Model. Because of the differences in size, shape, and weight from mines, munitions exhibit both variable responses to ambient coastal dynamics and diverse modes of mobility. The UXO mobility model can predict the fate of munitions over the broad range of coastal diversity where UXO are known to exist. Additionally, mobility information can be used to support a risk assessment by identifying the areas and entombment depths likely to contain munitions, thus reducing costs associated with fieldwork focused on physically locating or clearing munitions items. The ultimate goal is to incorporate munitions mobility and burial model output data into a risk assessment model, similar to the Army Risk Assessment Modeling System (ARAMS). To date, this model has been validated for trailing edge, collision coastline and biogenic coastal types under relatively benign conditions.

Several mobility studies have also been completed that gathered site specific data. SEA Engineering conducted mobility studies at Adak, Alaska, Mare Island, California, and Augusta Bay, Sicily. Similar to the approach used for contaminated sediment sites, these studies focused on mobility of sediments in which munitions were located. Where possible, site specific measurements were used, including sediment cores for geotechnical and radioisotope analysis, current and wave measurements, and wave, hydrodynamic, and sediment transport modeling. The researchers determined quantitative risk of munitions mobility and developed maps of risk for each type of munitions so that a remedial design could be undertaken if necessary.

In addition, the Army Corps of Engineers Engineer Research and Development Center (ERDC) conducted an ordnance migration study at Lake Erie near the Toussaint River, OH. The researchers deployed surrogate munitions and tracked their movement, and found ice was the major factor influencing movement in that environment.

Several munitions mobility knowledge gaps were identified. The group recommends modeling additional coastal types and an entire reef system or island. ESTCP has funded a new start project *Vortex Lattice UXO Mobility Model for Reef-Type Range Environments* (MM-1003) to apply the UXO Mobility Model for reef environments. This project will include reef geomorphology in the model grid, allowing prediction of munitions migration and burial in a reef environment without reliance on dense Light Detection and Ranging (LiDAR) bathymetric grids that limit the model’s computational domain. Extreme storm events have not yet been validated and should be studied. The group also recommends the mobility model should consider abrasion and bioaccretion as inputs, in addition to the existing model parameters.

2.2 MUNITIONS CORROSION PREDICTION

Little data exists on the state of corrosion of munitions on land and underwater environments. Understanding the condition of munitions casings will help characterize the potential for energetic fill material to move into the environment.

The UXO Corrosion Prediction Model, developed under the NESDI program, addresses corrosion in the underwater environment. This model provides an estimate of the time to perforation of munitions casings exposed to seawater. The model considers three types of exposure scenarios including ordnance items buried in sediment under seawater, partially buried and partially exposed to seawater, and fully exposed to seawater.

The corrosion prediction model provides a more accurate estimate of time to perforation for specific ordnance items versus non-specific ordnance items. This discrepancy in accuracy is related to the fact that time to perforation for specific ordnance items were obtained from detailed laboratory tests of these casings while estimates for non-specific ordnance items were obtained from field testing of steel in seawater and other theoretical considerations based on the metal types.

The model estimates time to perforation under ideal conditions and does not take into account abrasion or scour, exposure to air during low tides, dents and scratches or other physical damage to the casing, adjacent or touching metals, and water or substrate qualities such as temperature, pH, or Redox potential.

The group agreed it would be valuable to gain further information on the condition of munitions in the field. They recommended photographing recovered items during field operations to document their condition to support future research. Recovered items from the Ordnance Reef study in Hawaii were identified as good initial candidates for data collection.

2.3 MUNITIONS CONSTITUENTS (MC) RELEASE RATES

Estimating the amount of MCs released to the environment from both individual munitions and all munitions at a site over time is a crucial component of any risk-based site conceptual model, necessary in developing a scientifically defensible basis for predicting and assessing potential impacts from underwater MCs.

Researchers under SERDP project *Defining Munitions Constituent Source Terms in Aquatic Environments on DoD Ranges* (ER-1453) are working to develop a scientific basis for quantitatively estimating the source terms associated with breached or broken projectile casings, along with the fate and transport of MC contamination in the aquatic environments on DoD ranges. Specifically, researchers are developing a predictive modeling capability of MC fate and transport associated with an unexploded breached projectile as shown in Figure 2.

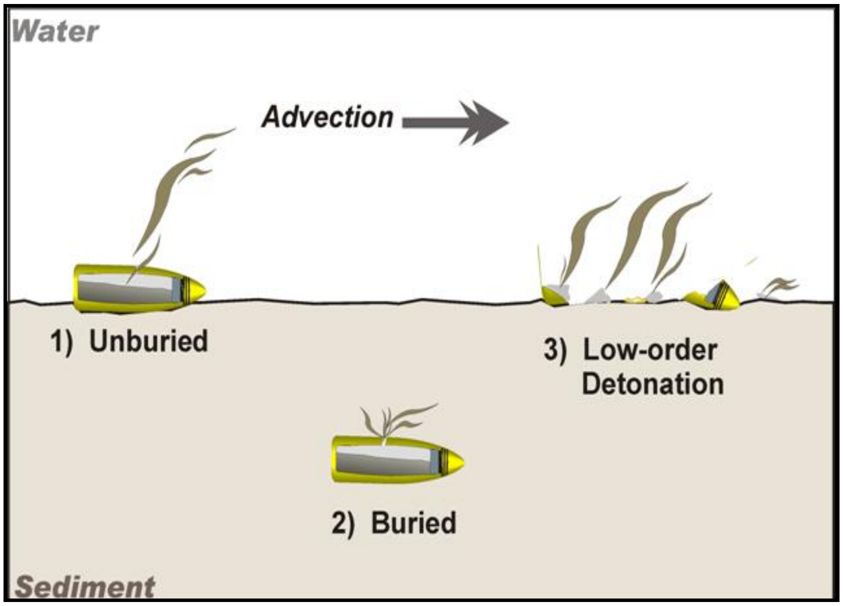

Figure 2. Release of MCs from munitions in the underwater environment

Empirical determinations are made of MC time-dependent transport out of surrogate munitions and MC mass depletion based on various states of shell integrity and hydrodynamic conditions. Researchers are evaluating interactions between the physicochemical characteristics of MCs and the physical forces associated with the aquatic environment to which MCs are exposed. The fate and transport modeling effort consists of defining and compiling input parameters to characterize the source release process through a release function and simulation of MC fate and transport under realistic conditions that correspond to DoD underwater munitions areas.

The release model depends on five variables, including ambient current speed, breach hole size, volume of cavity, dissolution rate of MC, and a hydrodynamic mixing coefficient. Probabilistic modeling capability has been developed which accounts for the uncertainties and variability associated with the five model parameters. The model can be applied for MC in solid or liquid form.

To date, simulated results compare well with the analytical results for both the release rates in water column and in-cavity concentrations. Release rates are governed by the hydrodynamic mixing through the breach hole, which are related to the ambient current speed and the hole sizes/shapes, as confirmed by the results. Based on the predicted release of TNT from one single shell, a fate/transport model has been used to simulate steady-state TNT concentration in San Diego Bay.

Additional work might focus on how to integrate the effects of multiple shells with varying shell and breach hole sizes into the model. There was discussion of using probability-based modeling approaches, such as Monte Carlo, to quantify these accumulated effects. The group suggested choosing a worst-case site and conducting some sediment and water column measurements.

2.4 MUNITIONS CONSTITUENT FATE AND TRANSPORT

Munitions casings underwater eventually breach and release MC and these compounds can be adsorbed on sediment, dissolve into the overlying waters, or bind to particles and be resuspended into the overlying waters. Over time, various chemical, biological, and physical processes change the MC to other chemical forms that have different transport and toxicity properties in various ecosystems. Although much work has been conducted on MC transformation in terrestrial and groundwater systems, little information is available on rates of attenuation or transport of energetics in coastal aquatic systems. This information is needed to support future risk assessments and site management decisions.

Several studies have been dedicated to the development of predictive models of MCs in the underwater environment. Modeling first requires developing a conceptual site model that includes all processes involved in the transport and transformation of munitions and MCs and that can predict spatial and temporal fate under different scenarios. In addition, laboratory experiments have been conducted to determine various model parameters.

Modeling requires knowledge regarding various aspects of the site. First, it is important to gather information on the source of contamination such as types of munitions present, if the munitions are buried, partially buried, or proud, and if they are intact. Additionally, information such as quantity and nature of energetics, dissolution rates, solubility, sorption and desorption data is needed. Abiotic degradation and transformation data is needed including hydrolysis and photolysis rates, and knowledge of the present metals. Finally, it is important to identify bacteria (aerobic and anaerobic) and fungi that could support biotic transformations.

Although several studies to date have dealt with modeling fate and transport of pollutants in terrestrial environments, little is known on modeling the fate of MCs in the underwater environment. One of the anticipated problems in predicting the fate and transport of MCs in water is the dynamic nature of the system. A second difficulty may arise from the size and the open boundaries of water bodies which hampers the detection of MCs and, hence, the validation of models in the field.

Fate and transport modeling capabilities can be advanced by gathering information to address a number of knowledge gaps. Group discussion focused on potential parameters for new models, which are provided in Table 1 by model parameter.

Table 1. Munitions Constituent Fate and Transport Knowledge Gaps.

Model Component	Knowledge Gap
Source Characteristics	• Munitions exposure- buried, partially buried, or proud • Munitions integrity- intact or ruptured
Site Characterization	• Better sampling tools that allow collection of samples/data under in-situ conditions (e.g. anaerobic samples) • More sensitive analytical tools suitable for on site detection (ppt levels) • Complete characterization of the site to be studied

Table 1. Munitions Constituent Fate and Transport Knowledge Gaps (continued).

Model Component	Knowledge Gap
Dissolution and Solubility	• Solubility as a function of temperature and salinity • Tides and waves data • Normalized dissolution rates under conditions that mimic the natural conditions (may be difficult to obtain) • Dissolution rates of MCs from formulations; dissolution from pure MCs differ from formulations
Sorption/ Desorption	• Correlation of sorption with organic and inorganic components (TOC, clays, metal oxides) to apply poly-parametric distribution models • Data on reversibility of sorption; in a large mobile body of water reversible sorption may be equivalent to no sorption • Interaction of particulate organic matter/ dissolved organic matter with MCs
Hydrolysis	• Generic constants such as Ea(OH) and lnA(OH) for all studied chemicals to predict the values of hydrolysis rate constants under various conditions
Photolysis	• Photolysis rate constants (k_v) measured with natural irradiation or solar simulator and related to the intensity of light and the salinity • Meteorological data (solar irradiation) • Variation of light intensity with the depth in water • Effect of dissolved organic matter (photosensitization, light absorption) • Interaction of particulate organic matter/ dissolved organic matter with MCs
Metals	• Normalized degradation rate constants (k_M) as a function of the amount and surface of the metal • Concentration of the metals in the underwater environment

2.5 ECOTOXICOLOGICAL EFFECTS OF MUNITIONS CONSTITUENTS

It is critical to accurately assess and prioritize the risks of explosive compounds to human and ecological health such that reasonable and effective remedial decisions can be made.

ERDC, U.S. Army Corps of Engineers and the Space and Naval Warfare Systems Center Pacific researchers have investigated the ecotoxicity of TNT, RDX, and HMX, along with their uptake, biotransformation, and elimination, in fish, mollusk and various other underwater marine life. The toxicity of explosives in sediments is also being assessed.

To date, the researchers have found that TNT is very reactive in exposure media and biota and RDX and HMX are much more stable. They found the MC elimination rate is high and bioconcentration and trophic transfer potential are low for all compounds. Results show these compounds are toxic at relatively high water and sediment concentrations. TNT, 2-ADNT, and RDX are toxic in the low mg/L (ppm) range, 2,4-DANT is not toxic at high concentrations, and HMX is not toxic at its solubility limit. These findings indicate environmental risks associated with their presence in marine environment may be negligible.

Additional ecotoxicity research has been conducted using a realistic exposure approach. Amphipods, polychaetes, and adult and embryonic mussels were placed in a tank with surface or buried explosives (Composition B fragement) or no explosive and exposed to dynamic and static

flow water conditions. The results of this research show that gentle flow conditions that would be found in low energy field sites reduce exposure to organisms inhabiting the vicinity of munitions and MC, due to simulated advection. Burial of the explosive virtually prevented movement of explosives to the overlying water, and therefore, reduced exposure risk to epibenthic and pelagic receptors. Fine-grained sediments have a strong decreasing effect on the overlying water and porewater concentrations of Composition B explosives. The relatively high sensitivity of TNT to mussel embryos make them a potentially good assessment tool at sites contaminated with TNT. These results also indicate the environmental risks associated with breached, leaking underwater UXO in the marine environment may be negligible.

Several knowledge gaps were identified by the group for the ecotoxicity of munitions constituents and include:

- Sublethal effects of explosives to marine fish and invertebrates
- Nature and toxicological role of TNT bound residues
- Influence of UV light on toxicity of explosives
- Limited toxicity data for some constituents and associated transformation products
- Environmentally relevant exposure concentrations

3.0 REQUIREMENTS FOR INTEGRATED FIELD DATA COLLECTION EFFORT

Reliable data from the field is required to conduct defensible risk assessments in the underwater environment. The group agreed it would be valuable to conduct several data collections on real munitions response sites and utilize the data to perform risk assessment studies at each site. The group envisions conducting each of the modeling studies in parallel using the water, sediments, and tissue data, and compiling the results to support risk assessment findings. The recent data collections, funded by the Army, at two sites in Hawaii can be used as a foundation for future studies.

The group discussed the need to develop a standardized approach to data collection that can support all components of future risk assessments. Table 2 provides a rudimentary framework for a standardized approach to data collection that is not meant to be comprehensive and should be expanded upon. Specific field data collection requirements on the left column of the table are matched with modeling studies these requirements would potentially support using an “X”. The data collection requirements are categorized by physical munitions, munitions constituents, physical characteristics of the site, and information on receptors in the study area. Table 2 illustrates how, in many cases, one measurement in the field supports multiple modeling studies.

Table 2. Rudimentary Framework for a Standardized Approach to Underwater Munitions Site Data Collection

Data Collection Requirement Category	Data Collection Requirements	Mobility Prediction	Corrosion Prediction	MC Release Rates	MC Fate and Transport	Ecotoxicology
Source Characteristics **Munitions**	Munitions type	X	X	X	X	X
	Spatial distribution of items on bottom	X			X	
	Location of items on seafloor (i.e. buried, partially buried, proud)	X	X	X	X	
	Condition and composition of munitions (i.e. corroded, rusted, intact, or ruptured)		X	X	X	X
	Shape of ruptured munitions opening		X	X		
	Water depths for most items in area of interest	X		X	X	X
Source Characteristics **Munitions Constituents**	Munitions constituent type			X	X	X
	Rate of release, period of release and spatial distribution of released agent			X	X	X
	Physical, biological, and chemical properties affecting fate and transport (i.e. hydrolysis half-life, aqueous solubility, vapor pressure, dissolution and solubility, sorption/desorption, etc.)			X	X	X
Physical Characteristics of the Sites	Range of bathymetry in site area	X				
	Types of sediment on seafloor (i.e. sand, silt, clay, etc.)	X		X	X	
	Seafloor features (environmental or manmade)	X			X	
	Water temperature and salinity	X	X	X	X	
	Hydrography including current and flow direction at various depths	X		X	X	X
Receptor Information	Identify if area is used for recreational or commercial fishing					X
	Identify surface-feeding birds, mammals, and migratory species					X
	Identify pelagic marine life					X
	Identify bentho-pelagic marine life					X
	Identify benthic marine life					X

The group also provided the following general recommendations on field data collection efforts:

- Recommend photographing recovered items. These photos can provide valuable information on munitions conditions. Specifically this information could help support corrosion and MC release studies.
- Recommend investigating analytic approaches utilized internationally for munitions response and domestically for radioactive sites to identify processes that could be applicable to an underwater munitions risk assessment.
- Consider conducting the field data collection studies on sites that have good ecological indicators and potential vulnerability to pollutants such as a coral reef ecosystem.

4.0 PRIORITY RECOMMENDATIONS

This section presents top level recommendations in the area of munitions in the underwater environment to improve the modeling capabilities and data sources, and to ultimately help support future site risk assessments and site decisions.

- Recommend field data collections on several worst-case munitions response sites, utilizing the data to support ecological risk assessment studies at each site using available components. Collect data on water, sediments, and tissue to support all aspects of the assessment. Conduct modeling studies in parallel and compile the results to support the overarching risk assessment findings. Build off recent data collections funded by the Army at two sites in Hawaii.
- Recommend developing a standardized approach to field data collection at underwater sites, collecting data in single efforts to support all components of comprehensive risk assessments.
- Recommend increased communication between the agencies and Services investing in research, development and demonstrations related to munitions in the underwater environment. Information exchange through periodic forums such as meetings, workshops, or conference calls is encouraged.

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